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Behavior of Cu(P) and Oxygen Free High Conductivity Cu Anodes under Electrodeposition Conditions

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ABSTRACT

Films formed on Cu(P) (with 0.1 atom percent P) and oxygen free high conductivity Cu anodes in electroplating solutions were studied by a newly developed gravimetric technique, electrochemical methods, x-ray photoelectron spectroscopy, and x-ray absorption spectroscopy. The black film formed on Cu(P) in Cl^--containing solutions was found to resemble a porous sponge composed of CuCl but laden with concentrated $CuSO_4$ solution. The gravimetric experiments show that the difference between the buoyancy-corrected measured mass change and the charge-equivalent mass change has two components: a reversible part that comes and goes as the current is turned on and off, and an irreversible part that remains on the surface and increases in mass with time as dissolution proceeds. The reversible part of the mass change arises from the weight of the diffusion layer. The irreversible part results from the anodic film, which increases linearly in mass with charge density but at a rate that is independent of current density. P inhibits the disproportionation of Cu^{+1} that results in the poorly adherent anodic film that forms on OFHC Cu anodes.

Anodes used in electrodeposition of Cu from acid-copper baths typically contain about 0.1 atom percent (a/o) P. This small amount of P has been shown to have a large effect in promoting the formation of an adherent black film on the anode surface during plating.[1,2] In contrast, pure Cu forms a brownish film (sometimes called slime), which is not adherent and can migrate to the cathode and degrade the plated film.

Copper is commonly electroplated from solutions containing H_2SO_4 and $CuSO_4$ with small amounts of Cl^-. The Cl^- has a strong influence on the deposition kinetics and deposit morphology.[3,4] Whereas classic studies of Cu dissolution and deposition in solutions of H_2SO_4 and $CuSO_4$ have determined that the reaction involves two consecutive charge-transfer steps with Cu^{+1} as an intermediate,[5,6] some reports have indicated that the second step of the dissolution process might involve disproportionation of Cu^{+1} [7]

$$2Cu^{+1} \rightleftharpoons Cu^{+2} + Cu \qquad [1]$$

The slime formed on pure Cu anodes in plating solutions containing Cl^- has in fact been attributed to disproportionation of some amount of Cu^{+1}. [1,2] It is known that Cl^- stabilizes Cu in the +1 oxidation state by forming various cuprous chloride complexes.[8-11] Despite being a small part of the overall dissolution reaction, the film formation reactions can have important consequences in electrodeposition applications because large charges are passed through a given anode. It has been suggested that the role of P is to promote oxidation of Cu directly to cupric ion, thereby avoiding the deleterious consequences of cuprous ion disproportionation.[1,2] The goal of the present work is to improve the understanding of the role of P and the behavior

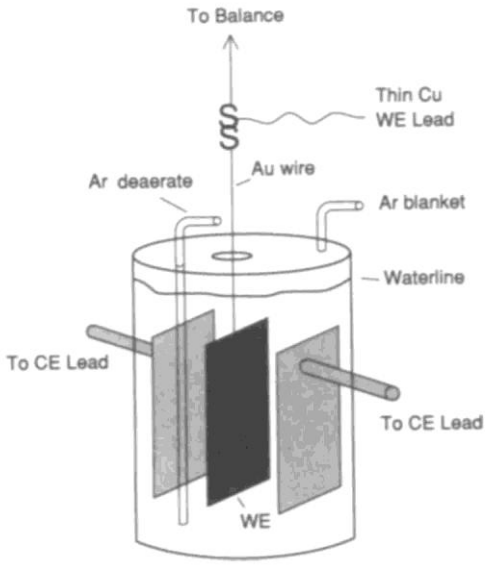

Fig. 1. Schematic representation of cell used in gravimetric experiments.

of the black anodic film. It should be emphasized that the plating reaction at the cathode was not a subject of this investigation.

Experimental

The electrolyte was a typical acid-copper plating solution consisting of 0.27*M* $CuSO_4$ + 1.7*M* H_2SO_4 + 2 m*M* HCl. In certain experiments, the $CuSO_4$ or HCl was omitted. Samples of Cu-0.1 a/o P and oxygen free high conductivity (OFHC) Cu were anodically polarized, usually at constant current in the range of 15-30 mA/cm^2. This range is typical for anodic current density during electrodeposition of Cu from acid sulfate baths.

In order to study the behavior of the anodic films, it was necessary to develop a sensitive, *in situ* gravimetric technique. The technique needs to be sensitive since film formation is a small part of the overall dissolution process. In order not to disrupt the fragile surface films, it is important to have *in situ* measurement capability. The gravimetric technique used is a modification of previously described methods.[12-15] Hurlen suspended samples from a quartz helix and monitored the mass change, as determined by the helix contraction, during exposure to

solutions with a range of oxidizing power.[12-14] In this work, the samples were suspended from a hanging balance, and current was provided to the sample by means of an electrical connection, Fig. 1. A similar technique has been used to determine potentials of zero charge of a gold foil in various electrolytes.[15] The balance used in this work was a Cahn DCA-312, which has automatic data acquisition, a minimum time resolution of 1 s, and a sensitivity of 0.1 mg. The samples were $2.5 \times 5 \times 0.25$ cm^3 sheets (with total area of about 28 cm^2) that were abraded to 600 grit and suspended in the solution by a 0.025 cm diam Au wire passing through a small hole drilled in the samples. The Au wire intersected the water line and was connected to the balance by a Cu S-hook. Electrical connection was made with a 0.012 cm diam Cu wire that was attached to a second S hook. This thin Cu lead did not influence the measured weight change. Two Cu counterelectrodes equal in area to the sample were used. A PAR 273 potentiostat was used for these experiments, and the current was recorded by a PC/AT computer. The current was turned on for periods of 5, 15, or 60 min, which were separated by periods of 5 min with the current off. The 100 ml cell was glass and had a cover with a hole allowing passage of the Au wire and connections for deaeration and blanketing of the electrolyte with wet Ar gas.

In most gravimetric experiments, the solution was agitated by bubbling wet Ar at a rate of 50 sccm through a 3 mm diam open-ended glass tube immersed in the cell. The solution separated for large current densities and large charge densities in the absence of such agitation, as dark solution settled to the bottom and clear solution remained at the top of the cell. Bubbling, with Ar eliminated this artifact while introducing minimal noise in the measured mass. Even though Ar bubbling does not produce well-defined mass transport conditions, the data were quite reproducible. It should be noted that the extent of mixing was certainly greater than that provided by natural convection. The diffusion-layer thickness for these conditions of Ar bubbling in the gravimetric cell was determined to be about 120 μm from the limiting current density at an Ni electrode in a solution of 1.5*M* NaOH + 0.15*M* $K_3Fe(CN)_6$ + 0.15*M* $K_4Fe(CN)_6$.[16] The actual diffusion-layer thickness in the plating solution will be somewhat different because of viscosity and density effects. Furthermore, there may be some variation along the length of the sample. Nonetheless, 120 μm can be used as an approximate value. For stagnant experiments, the solution was blanketed with wet Ar to prevent evaporation.

Anodic films formed on OFHC Cu and Cu(P) were examined by x-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS). Samples for XPS analysis were prepared by anodic polarization at a constant current of 30 mA/cm^2 for 90 min. Following this treatment, the Cu(P) samples were gently washed with water and dried with N_2. The OFHC Cu samples were just left to dry, since washing with water resulted in complete removal of the brown film.

XAS was done in transmission on samples prepared by two different methods. In the first approach, a Cu(P) sheet was anodically polarized for several hours in a beaker containing the complete plating solution. The sample was removed, and black film was immediately scraped off the anode surface with no prior rinsing. This material was then sealed in polyimide tape and analyzed. In the second approach, the XAS analysis was performed *in situ* without removing the sample from the cell. Cu(P) and OFHC Cu pieces were first thinned to 0.01 cm by rolling. A 300 Å thick film of Pt was evaporated on one side of each sample to assure conductivity. Each was then totally converted to anodic film by electrodissolution in a solution containing H_2SO_4 and HCl only (with no $CuSO_4$). The plastic cell had a narrow (0.07 cm) crevice region, attached on one side, in which the sample was dissolved, Fig. 2. In this configuration, the x-ray beam only needed to pass through a small amount of solution. Furthermore, the force of gravity caused the

dense copper containing solution generated by dissolution of the anode to drop down to the bottom of the cell. This technique allowed analysis of the copper in the anodic film with no contributions from underlying copper metal or copper in solution. The x-ray energy was scanned in steps of 5, 0.5, and 5 eV in the ranges −100 to −10, −10

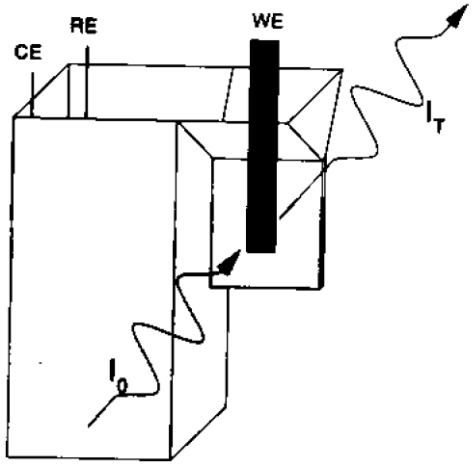

Fig. 2. Schematic representation of cell used for *in situ* XAS experiments.

to +50, and +50 to +200 eV, respectively, where the ranges are given relative to the Cu K edge at 8982 eV. The absorption coefficient was taken to be ln (I_0/I_T), where I_0 and I_T are the incident and transmitted beam intensities as measured by ionization chambers. The background decay of each edge was subtracted out by fitting a line to the region below the edge. The edges were then normalized to a step height of unity using the data from 100 to 200 eV.

Rotating ring-disk electrode (RRDE) experiments were performed with both Cu and Cu(P) disks in an assembly that allowed for removal and exchange of the disk. The Pt ring was potentiostated at 0.3 V *vs.* a saturated mercurous sulfate electrode (MSE) so as to monitor the rate of Cu^{+1} release from the disk by its oxidation to Cu^{+2}. The solutions were deaerated by bubbling with N_2 prior to the experiments and blanketed with N_2 during the experiments. The disks were 0.5 cm in diameter, and the collection efficiency at the ring was 22%. The disks were abraded to 1200 grit prior to measurement. The rotation rate was 350 rpm. A Pine Instruments rotator and potentiostat were used for the RRDE experiments. The disk was kept at open circuit for 10 min and then polarized anodically for 15 min at a current density of 15 mA/cm^2 (2.8 mA).

Potentiodynamic polarization curves were measured with the Cu and Cu(P) disks in the RRDE assembly. The rotation rate was 350 rpm. A PAR 273 potentiostat was used with the current-interrupt IR compensation option. The reference electrode was a MSE electrode capacitatively coupled to a Pt wire. The potential was scanned anodically from open circuit at a rate of 0.1 mV/s.

Analysis of Gravimetric Data

During anodic dissolution, the anode may be assumed to be a two-phase composite consisting of a metallic phase and a homogeneous anodic film phase. The measured mass change

will be a sum of the mass changes of the two phases corrected for buoyancy effects

$$\Delta m_{meas} = \Delta V_m(\rho_m - \rho_s) + \Delta V_f(\rho_f - \rho_s) \qquad [2]$$

where ΔV_m and ΔV_f are the volume changes of the metal and anodic film phases, respectively, and ρ_m, ρ_f, and ρ_s are the densities of the metal, film, and solution, respectively. The anodic film thickness, $\Delta x_f = \Delta V_f / A$ where A is the total electrode area, can be shown by rearrangement of Eq. 2 to be

$$\Delta x_f = \frac{1}{A}\left(\frac{\rho_m - \rho_s}{\rho_f - \rho_s}\right)\left[\frac{\Delta m_{meas}}{(\rho_m - \rho_s)} - \Delta V_m\right] \qquad [3]$$

However, from Faraday's law the volume change of the metal is proportional to the charge passed, Q

$$\Delta V_m = \frac{M_m}{\rho_m n F}\int_0^t I(\tau)d\tau = \frac{M_m Q(t)}{\rho_m n F} \qquad [4]$$

where t is time, M_m is the atomic weight, n is the number of electrons per atom of dissolved copper, and F is Faraday's constant. No side reactions such as gas evolution would be expected to occur at the anode surface. The value of n was determined for each experiment from the total charge and total mass loss, which was measured at the end of the experiment after removing the anodic film by ultrasonic cleaning in water. This approach determines an average value of n, which is assumed to be constant during the entire experiment (an assumption that may be in error).

It is now convenient to define two area-normalized masses: the measured mass change corrected for buoyancy, $\Delta m_D = \rho_m \Delta m_{meas}/A\ (\rho_m - \rho_s)$, and the charge-equivalent mass change, $A m_E = M_m Q\ (t)/AnF$. The anodic film thickness (and also film mass, since $\Delta m_f = A\Delta x_f \rho_f$) is thus proportional to the difference between the buoyancy-corrected measured mass change and the charge-equivalent mass change

$$\Delta x_f = \frac{1}{\rho_m}\left(\frac{\rho_m - \rho_s}{\rho_f - \rho_s}\right)[\Delta m_D - \Delta m_E] \qquad [5]$$

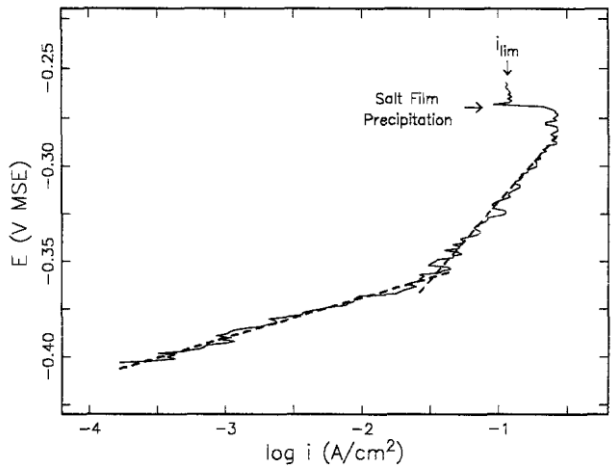

Fig. 3. Potentiodynamic polarization curve for Cu(P) rotating disk in 0.27*M* $CuS0_4$ + 1.7*M* H_2SO_4 + 2 m/*M* HCI. Fitted Tafel slopes are shown as dashed lines.

The solution density was measured to be 1.131 g/cm^3, and ρ_m was taken to be that of copper, 8.96 g/cm^3. The apparent density of the black film was determined by scraping the anodic film off a Cu(P) sample that had been freshly anodized in a Cl^- containing solution, filling a known length of 0.76 mm diam Teflon tube, and measuring the mass change. The average value of several measurements were 1.4 g/cm^3. Using these values, the factor in Eq. 5 relating anodic film thickness to the difference between buoyancy-corrected measured mass and current-equivalent mass is 32.5 μm-cm^2/mg. It was not possible to measure the density of the brown film formed on pure Cu because of its lack of cohesion. The densities for the thin anodic films formed on both Cu and Cu(P) in solutions without Cl^- were not determined.

Results

Potentiodynamic polarization experiments.—The polarization curve for Cu(P) in the full electrolyte is shown in Fig. 3. The fluctuations in the current are probably caused by a noisy brush contact to the rotating disk. At −270 mV, a current drop resulting from salt film precipitation is exhibited. The exchange current density for the Cu/Cu^{+2} reaction, as determined by extrapolation to the open-circuit potential, is 0.3 mA/cm^2. Two Tafel slopes are seen: 21 mV/dec at low overpotentials and 83 mV/dec at higher overpotentials. If the direction of the potential scan is reversed before salt film precipitation occurs, the current traces back almost exactly along the same curve with little hysteresis, indicating that the two Tafel slopes represent two activation-controlled regions. During such a potential cycle to high current densities, considerable black film forms on the surface. Since the current on the reverse scan is unaffected, the black film does not appear to impede the dissolution process.

XPS and XAS experiments.—XPS analysis of a black film formed on Cu(P) in CI^- containing solution showed the presence of the following elements in the respective oxidation states: Cu, +1; O, −2; CI, −1; P, 0 and +3. The P/Cu ratio was 9 a/o after 160 C/cm^2 and increased with increasing charge; this is an increase of 100 times that in the metal. The Cl/Cu ratio was 25%. The energy of the Cu LVV Auger line indicated that CuCl was the major

component. Additionally, there was evidence of some Cu_2O, which may result from reaction with air during sample transfer.

X-ray absorption spectra at the Cu K edge are given in Fig. 4 for metallic Cu and several different Cu containing compounds. The edge moves to higher energies as the oxidation states increases. A pronounced peak at the edge is seen for $CuSO_4$. Similar absorption edges of Cu containing compounds have been previously reported.[17,18] The absorption edge for black film material scraped off an anode is shown in Fig. 5; it appears to be a combination of CuCl and $CuSO_4$ edges.

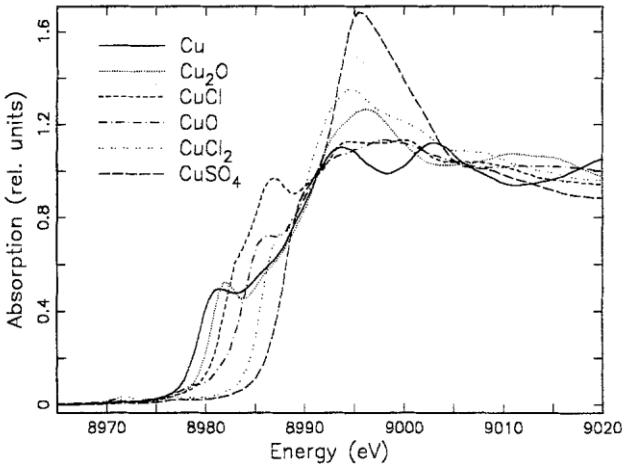

Fig. 4. Absorption edges of Cu and Cu containing compounds.

The absorption edge of a black film formed in the cell shown in Fig. 2 using the method described above is given in Fig. 6. This film, which has been totally converted from a thin Cu(P) foil in a solution without $CuSO_4$, exhibits an absorption edge very similar to CuCl. The rather large amount of P in the film may be responsible for the variations from the CuCl edge. These observations indicate that the black film is similar to a porous sponge that is composed of CuCl and saturated with concentrated $CuSO_4$ solution. The difference between the samples of Fig. 5 and 6 is that the black film scraped off a sample polarized in the full plating bath is actually a combination of the film and the solution. By dissolving a thin foil in a solution without $CuSO_4$, however, only the substance of the black film, or a CuCl-like material, is present.

The brown film formed by a similar treatment of a thin OFHC Cu foil in a solution with no $CuSO_4$ appeared to be a combination of Cu and CuO. This XAS observation is in agreement with XPS analysis of the brown film on Cu, which also found metallic Cu in the anodic film. Since the sample was not rinsed prior to XPS analysis, and thus dried $CuSO_4$ was present on the surface, Cu^{+2} and S were also observed. In the absence of P, Cu^{+1} likely disproportionates to result in a fine mixture of Cu in the 0 and +2 oxidation states. The P inhibits the disproportionation reaction.

Gravimetric experiments.—The gravimetric experiments provided further information on the nature of the anodic films. In Fig. 7, both the buoyancy-corrected measured mass change, Δm_D, and the charge-equivalent mass change, Δm_E, are shown for the first part of an experiment

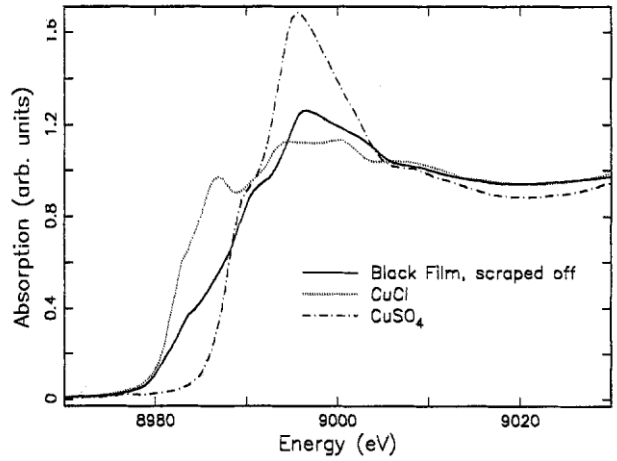

Fig. 5. Absorption edge of black film scraped off of an anode and encapsulated in tape along with selected standards.

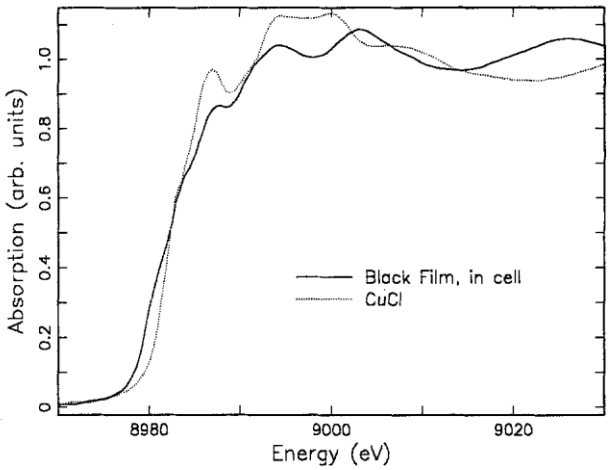

Fig. 6. Absorption edges of CuCl and *in situ* black film formed by total conversion of Cu(P) foil.

during which a current of 30 mA/cm^2 was periodically applied to a Cu(P) electrode in Cl^- containing solution. If the current causes faradaic dissolution of Cu, the metal should lose mass at a constant rate when the current is on, and the mass should be constant when the current is off. This behavior is displayed by Δm_E in Fig. 7. As seen from Δm_D, however, the sample mass actually increased when the current was first turned on (at the 5 min mark). After about 30 s, a maximum mass was achieved and the sample then lost mass at a constant rate, with a slope close to that exhibited by Δm_E .When the current was turned off 15 min later, the sample continued to lose weight for several minutes. The difference between Δm_D and Δm_E, shown above to be proportional to the anodic film mass, is given in Fig. 8 for an extended experiment. The mass

change is seen to be composed of two parts: a reversible part, Δm_{Rev}, that came and went as the current was turned on and off, and an irreversible part, Δm_{Irr}, that remained on the electrode surface. The reversible mass change was relatively constant with time, but the irreversible mass change increased almost linearly with time. This behavior has been observed for experiments lasting up to 17 h.

The effects of both current density and charge density on the reversible and irreversible mass changes are shown in Fig. 9 for Cu(P) in Cl^- containing solution. The reversible mass change increases almost linearly with current density and is relatively constant with time or charge. The irreversible mass change increases linearly with charge density and is almost independent of current density.

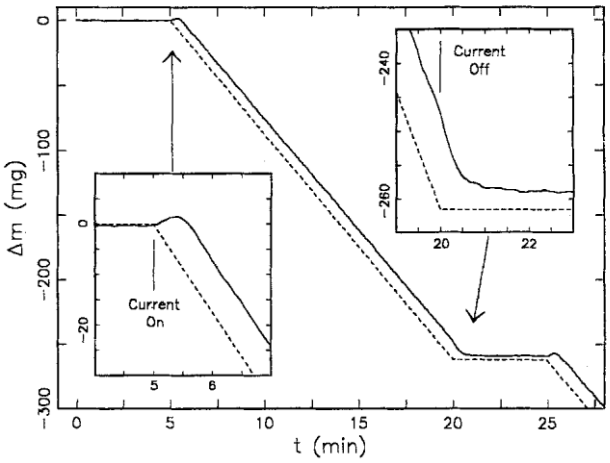

Fig. 7. Buoyancy-corrected measured mass change, Δm_D. (solid line), and charge-equivalent mass change, Δm_E (dashed line), for the initial part of an experiment with Cu(P) in agitated Cl^- containing solution at 30 mA/cm^2.

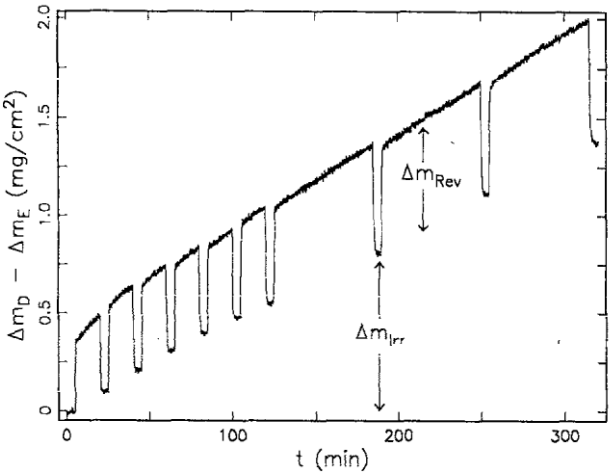

Fig. 8. Difference between Δm_D and Δm_E for the same experiment as Fig. 7. The current was turned on for periods of 15 and 60 min separated by periods of 5 min with current off.

A comparison of stagnant and agitated experiments is shown in Fig. 10 for the lowest current density studied, 15 mA/cm^2. Whereas both the reversible and irreversible mass changes decrease with agitation, the irreversible mass change is more strongly affected.

Similar experiments (with agitation) were performed using Cu(P) in solutions without Cl^- and using OFHC Cu anodes in solutions both with and without Cl^-. The reversible mass changes were similar for all cases, also varying at the end of the first 15 min period between 0.2 and 0.4 mg/cm^2 for current densities between 15 and 30 mA/ cm^2. The films formed on both Cu and Cu(P) in CI^- containing solutions exhibited reversible mass changes that increased weakly with charge density. The irreversible mass changes were also similar for all cases except Cu in CI^- containing solutions. The slopes of the Δm_{Irr} *vs.* charge density curves are given in Table I. For Cu in Cl^- containing solutions, the irreversible film mass was found to increase about ten times faster than for the other cases.

The physical nature of the anodic films for the various cases was found to be vastly different. In contrast to the thick, viscous black film formed on Cu(P) in the presence of Cl^-, the brown film formed on OFHC Cu adhered poorly to the electrode surface. As soon as the electrode was handled, the brown film would easily dislodge from the surface. A light stream of water was sufficient to completely remove the film. In solutions without Cl^-, the anodic films formed on both Cu and Cu(P) were much thinner, and the underlying metallic grains could be seen through the films. In the absence of Cl^-, the film formed on Cu washed off easily, but the film on Cu(P) was difficult to remove completely even by ultrasonic cleaning in water.

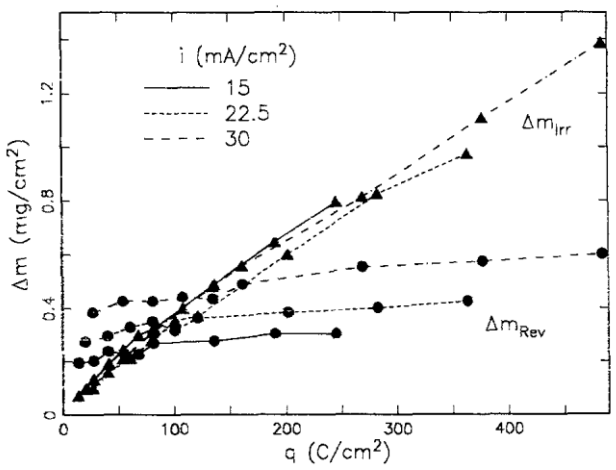

Fig. 9. Influence of current density and charge density on reversible and irreversible mass changes for Cu(P) in agitated Cl^- containing solutions.

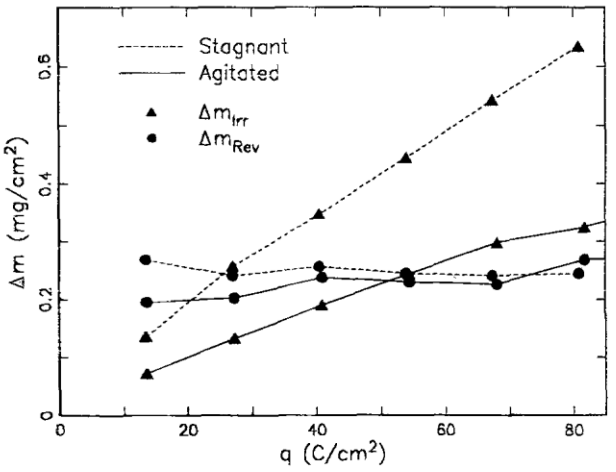

Fig. 10. Influence of agitation on mass changes for Cu(P) at 15 mA/cm^2 in Cl^- containing solutions.

The values of *n* determined after the gravimetric experiments are given in Table I. The values for Cu(P) may be somewhat high as a result of incomplete removal of the anodic film by the ultrasonic cleaning. This likely explains the apparent *n* slightly larger than 2 for dissolution of Cu(P) in the solution without Cl^-. The one case with an *n* much less than 2 was Cu in the Cl^- containing solution. The Cl^- stabilizes the cuprous ion by complexation, but it does not prevent the disproportionation reaction that results in thick slime formation on Cu anodes. In fact, disproportionation was enhanced in the presence of Cl^-.

RRDE experiments.—In the RRDE experiments, the current monitored at the ring, divided by the collection efficiency, measures the rate of Cu^{+1} release from the disk. (Note that whereas cuprous ions are likely complexed by Cl^-, they are designated here simply as Cu^{+1}.)

Experiments were performed on Cu and Cu(P) disks in solutions both with and without Cl^-. The disk was held at open circuit for 10 min and then anodically polarized at 15 mA/cm^2 for 15 min. Figure 11 shows the ring current during the last part of the experiment. The ring current measured at disk open circuit results from etching of Cu by Cu^{+2}, which is Eq. 1 in the reverse direction. Gravimetric experiments show that Cu and Cu(P) lose weight in the plating solution at open circuit in deaerated solutions at a rate equivalent to 4×10^{-5} A/cm^2. This weight loss results from the etching reaction. Similarly, it has been reported that Cu electrodes lose weight when they are polarized with small cathodic currents in H_2SO_4 + $CuSO_4$. [19,20] The rate of Cu^{+1} release is higher in Cl^- containing solutions and is higher for the Cu compared to the Cu(P) disk. The cuprous ion is complexed and stabilized by the chloride.

Upon anodic polarization of the disk, the ring current rises sharply and then decays. After the initial transient, the changes become slow. Ring currents after 15 min of disk polarization show the same relative trends as at disk open circuit but are different in magnitude. The ring current is higher in Cl^- containing solutions and with the Cu disk. The ring current for the Cu(P)

Table I. Slopes of irreversible mass change vs. charge density and values of *n* calculated after the gravimetric experiments.

		With Cl^-		Without Cl^-	
		Cu	Cu(P)	Cu	Cu(P)
$d(\Delta m_{irr})/dq$	mg/C	0.0203	0.00272	0.00170	0.00216
n	eq/mol	1.890	1.997	1.998	2.004

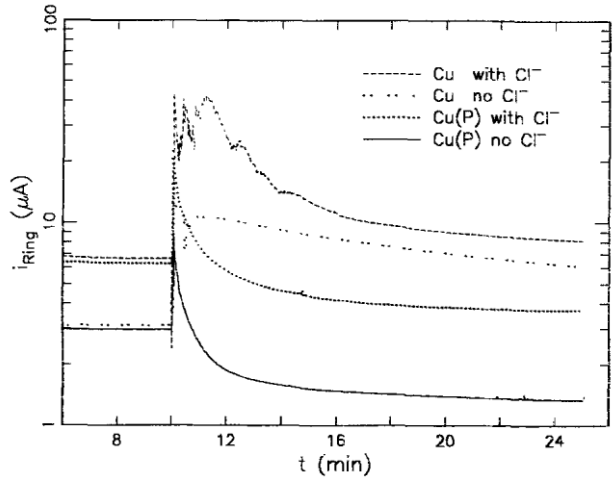

Fig. 11. Measured ring current Cu(P) and OFHC Cu disks in 0.27*M* $CuSO_4$ + 1.7*M* H_2SO_4 with and without 2 m*M* HCI. The disk was held at open circuit for 10 min at which time the disk was anodically polarized at 15 mA/cm^2 = 2.85 mA. Collection efficiency at the ring was 22%.

disk is lower after a few minutes of anodic polarization than when the disk is at open circuit. That is, the release of Cu^{+1} during etching by Cu^{+2} at open circuit is larger for Cu(P) than its

release during anodic polarization. It is important to emphasize that the ring current reflects only the Cu^{+1} released from the disk and is not necessarily equal to the rate of Cu^{+1} produced at the disk, since Cu^{+1} can be bound into the black film on Cu(P) or can disproportionate in the case of Cu anodes. The decrease in ring current with time suggests that the growing anodic film inhibits release of Cu^{+1}.

Discussion

Each of the experiments described above reveals an aspect of the nature of the anodic films formed on Cu and Cu(P). The current densities and potentials used in this study are well below the values at which salt film precipitation is observed as shown in Fig. 3. These films are therefore not salt films that precipitate on account of mass-transport limitations. In fact, a small amount of black film forms on the surface of Cu(P) during prolonged exposure at open circuit.

The gravimetric experiments show that the mass change has two parts: the reversible part that comes and goes as the current is turned on and off and the irreversible part that continually increases. Interestingly, this behavior was observed for anodic films on Cu and Cu(P) in solutions with and without Cl^-, films with widely varying chemical and physical characteristics. Such similarity suggests that Δm_{Rev} results from the dissolution process. During dissolution, a diffusion layer containing electrolyte more concentrated and denser than the bulk solution exists at the sample surface. The concentration in the diffusion layer will increase and decrease as an applied anodic current is turned on and off, in a fashion similar to the observed behavior of Δm_{Rev}. This dense diffusion layer adds to the mass of the sample, suggesting that Δm_{Rev} results from the increased weight of the diffusion layer. The gravimetric analysis presented above can be modified to account for a third contribution, the concentrated solution within the diffusion layer, to result in an equation similar to Eq. 5

$$\Delta m_D - \Delta m_E = \left(\frac{\rho_m}{\rho_m - \rho_s}\right) \{\Delta x_f(t)[\rho_f - \rho_s] + \Delta x_{dl}[\rho_{dl}(t) - \rho_s]\} \quad [6]$$

where Δx_{dl}, is the diffusion layer thickness (=120 μm) and ρ_{dl} is an average diffusion layer solution density. When the current is turned on or off, the anodic film does not change in thickness, and the change in $(\Delta m_D - \Delta m_E)$ or Δm_{Rcv} is a result of a change in the density of the diffusion layer as the concentrated cupric sulfate solution in the diffusion layer collects or diffuses away. Conversely, while the current is on, the diffusion-layer density reaches a steady-state value, and the change in $(\Delta m_D - \Delta m_E)$ reflects an increase in anodic film thickness, Δx_f, and an increase in Δm_{Irr}.

The magnitude of Δm_{Rev} can be calculated from Eq. 6 if several assumptions are made. The density of the plating bath saturated with $CuSO_4$ was measured to be 1.22 g/cm^3, which is 0.09 g/cm^3 larger than the density of the standard plating bath. A current density of 15 mA/cm^2 is 13% of the limiting current density shown in Fig. 3. If the surface concentration scales with the current density, the solution directly next to the electrode may be assumed to be denser than the bulk solution by 0.012 g/cm^3. Assuming a linear density gradient in the diffusion layer, the average difference between the diffusion layer and bulk densities is 0.006 g/cm^3. For these conditions, Eq. 6 predicts Δm_{Rev} = 0.1 mg/ cm^2, which is on the order of the observed value of 0.2 mg/cm^2.

Another calculation supports the view that the reversible mass change results from the diffusion layer weight. The diffusion layer thickness may be estimated from the Δm_D transient observed when the current is turned off (see inset in Fig. 7) using $x = (\sqrt{2Dt})$ and assuming $D = 5 \times 10^{-6}$ cm^2/s. This analysis results in a diffusion layer thickness of 122 μm, the same value as measured in the ferro/ferricyanide solution.

The irreversible mass change reflects the increasing mass and thickness of the anodic film. Taking the measured density of the black film, Δm_{Irr}. can be converted into thickness or volume change using the constant described above. The black film is thus 45.5 μm thick after a charge of 485 C/cm^2 has passed. The rate of mass increase of 2.72×10^{-3} mg/C is equivalent to a volume increase of 8.8×10^{-6} cm^3/C This is about 25% of the rate of metal loss. In other words, for every 1 μm of metal dissolved from the anode, 0.25 μm of black film will form. The densities for the anodic films other than the black film are not known. As a result, it is not possible to know the relationship of the mass changes to volume or thickness changes. The presence of metallic Cu in the brown film formed on Cu in Cl^- containing solutions likely increases the density of the anodic film substantially. Thus, although the brown film is 10 times heavier than the black film for a given charge density, it may even be thinner. In Cl^- free solutions, the anodic films are noticeably thinner on both Cu and Cu(P). The densities of these films are probably also higher than that of the black film, since the film masses increase at only a slightly slower rate than the black film mass.

The XPS and XAS experiments provide information on the composition of the anodic films. The black film on Cu(P) is enriched in P and Cl with Cu in the +1 oxidation state. It should be noted that no information was obtained on possible gradients of these species in the black film. There is no evidence that the black film acts as an impediment to current flow. Dissolved cupric ions can clearly pass through the black film at very high rates. The black film may be viewed as a porous structure made up of a CuCl-like material that is enriched with P. This notion is supported by the very low apparent density of the film compared to the density of 4.14 g/cm^3 for solid CuCl.[21] The cupric ions will attract sulfate anions to maintain charge neutrality, and this dissolved cupric sulfate permeates the film.

The ring current for Cu in H_2SO_4 + CuSO, + HCl is the equivalent to a Cu^{+1} current at the disk of 36.9 μA, which is far less than the 308 μA calculated from the measured value of *n*. Clearly, most of the Cu^{+1} disproportionates and is not released into solution. The ring current for the Cu(P) disk is close to the current calculated from the *n* value, indicating that almost all of the Cu^{+1} produced at Cu(P) anodes is released into solution. It should be noted that the hydrodynamic conditions in the gravimetric experiments during which *n* was measured differed from those of the RRDE experiments, and this might affect the release rate of Cu^{+1}.

The behavior of other P containing alloys in acidic solutions has been studied in recent years.[22-24] Hashimoto and co-workers studied P in amorphous Ni and Ni-Cr alloys and found that P does not dissolve in HCI at potentials below 200 mV SCE, and thus dissolution of the alloy results in the formation of an elemental P surface layer.[22,23] Virtanen *et al.* examined the behavior of amorphous Fe-Cr-P alloys and observed the presence of a black surface film containing P in the +5 oxidation state.[24] The alloys contained much higher levels of P than the Cu(P) alloy investigated here. However, the trends are similar and suggest that P has an effect, even at low concentrations, because it is enriched at the surface. For Cu(P), this leads to a constantly thickening anodic film.

The dissolution and film-formation mechanisms as well as the role of P and Cl^- can be assessed using the data presented above. Most of the dissolved copper oxidizes to the cupric state

via the cuprous intermediate as has been described several decades ago.[5,6] In the present work, an acid-copper solution containing a small amount of Cl^- was studied because of the use of Cl^- containing solutions in electrodeposition. Chloride complexes and stabilizes the cuprous ion so that the likelihood of oxidation to cupric is somewhat reduced.[8-11] The small percentage of the reaction that does not follow the first path, to dissolved cupric ions, has important consequences in electrodeposition applications since large charges are passed through a given anode. Under various circumstances, Cu^{+1} can be incorporated into the anodic black film, disproportionate to result in slime or be released into solution. Disproportionation is enhanced in the presence of Cl^- for a pure Cu anode because the lifetime of the cuprous species is increased. However, on Cu(P) disproportionation does not take place, even with 2 m*M* Cl^- in solution. The P is enriched at the surface, which probably reduces the catalytic activity. Disproportionation requires a catalytic surface as the homogeneous reaction is slow.[25] By poisoning the surface catalysis, P counteracts the influence of Cl^-, which is to promote disproportionation. The consequence of reduced disproportionation is that cuprous ions dissolving from Cu(P) tend to be either further oxidized to Cu^{+2} or incorporated into the anodic black film.

Conclusion

The films formed on anodes of OFHC Cu and Cu −0.1 a/o P in $CuSO_4 + H_2SO_4$ solutions with and without Cl^- were studied under conditions typical of anodes in Cu electrodeposition. The following conclusions can be made:

1. The black film formed on Cu(P) in Cl^- containing solutions contains Cu^{+1}, Cl, and P. It is envisioned to be a porous $CuCl^-$like matrix that is laden with aqueous $CuSO_4$ solution. The brown film formed on Cu contains CuO and metallic Cu as a result of Cu^{-1} disproportionation.
2. Gravimetric experiments indicated that the mass of the black anodic film formed on Cu(P) in plating solutions increases linearly with charge density in a fashion that is independent of current density.
3. The beneficial effect of P in Cu(P) is to inhibit disproportionation of Cu^{+1}.

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